BIOLEACHING OF COPPER ORES BY MEANS OF DIFFERENT CHEMOLITHOTROPHIC BACTERIA AND ARCHAEA

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ABSTRACT. Samples of copper ores from some essential Bulgarian deposits were subjected to bioleaching by means of different microorganisms (bacteria and archaea) isolated from these deposits. It was found that the isolated microorganisms were able to leach efficiently copper from the copper ores present in the deposits. High copper extractions (over 80 and in some cases over 90%) were achieved from all copper ores tested in these investigations by means of the mesophilic and moderate thermophilic bacteria at their optimum temperatures (about 35 and 50^{o}C, respectively) as well as by the extreme thermophilic archaea at temperatures higher than 75^{o}C.

Keywords: copper ores**,** leaching, chemolithotrophs, archaea

БИОЛОГИЧНО ИЗВЛИЧАНЕ НА МЕДНИ РУДИ ПОСРЕДСТВОМ РАЗЛИЧНИ ХЕМОЛИТОТРОФНИ БАКТЕРИИ И АРХЕИ

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РЕЗЮМЕ. Проби от медни руди от някои основни български находища бяха подложени на биологично излугване с помощта на различни микроорганизми (бактерии и археи), изолирани от тези находища. Установено бе, че изолираните микроорганизми са способни ефективно да извличат мед от медните руди, присъстващи в находищата. При всички медни руди, използвани в това изследване с помощта на мезофилни и умерени термофилни бактерии, (при оптималните им температури съответно около 35 и 50°C), както и с крайни термофилни археи (при температури над 75^{o}C) е постигнато високо извличане на медта (над 80 и в някои случаи над 90%).

Ключови думи: медни руди, излугване, хемолитотрофи, археи

Introduction

The ability of some chemolithotrophic bacteria and archaea to extract valuable metals from different mineral substrates (mainly sulphidic and mixed ores, concentrates and mineral wastes) is largely applied in several countries rich in such natural resources and/or industrial products. The first studies in this area in South Europe started in 1967 and within a relatively short period of time covered a large number of problems: the data about microflora of the different mineral deposits (such as ores of non-ferrous metals, uranium and gold; the investigations of the biochemistry and genetics of the microorganisms participating in the transformations of different mineral substrates such as coal, kaolin, oil, quartz sands, etc.; bioleaching of copper, other non-ferrous metals and uranium by means of heap, dump and in situ techniques; pre-treatment of gold and silver-bearing sulphide concentrates and ores by means of chemolithotrophic bacteria and archaea to expose these precious metals; combined microbial andchemical leaching of theprecious metals from the above-mentioned pretreated ores and concentrates, as well as from oxide ores; microbial removal of iron from quartz and kaolin, of sulphur from coal. Silicon from low-grade bauxites, and of phosphorus from iron ores; improvement of the ceramic properties of kaolin;microbial enhanced oil recovery; electricity production by means of microbial fuel cells.

The processing mentioned above isconnected with the participation of a large number of microorganisms, mainly of chemolithotrophic bacteria and arhaea. It is essential to mentionthat even the well-studied bioleaching of copper from low-grade ores is connected with the participation of several microorganisms related to different taxonomic species. At the same time, it must be noted that even microbial strains related to one and the same taxonomic species can differ considerably from each other with respect tothe level of their leaching ability and the optimum conditions for manifesting their ability.

The present paper contains some data about the microflora participation in the bioleaching of copper from the low-grade ores in some of the Bulgarian deposits subjected to such treatment.

Materials and Methods

Samples from some of the Bulgarian copper deposits connected with the application of bioleaching of the relevant ores were used in this investigation (Table 1). Some of these samples were inhabited by the local representatives of the microflora participating in the spontaneous and/or industrial bioleaching of the relevant ores.

Table 1. *Ore samples used in this investigation*

Ore sample	Source of the ore sample
№ 1	Low grade copper ore from the Vlaikovvrah deposit, with 0.53% Cu, 6.2% S, 7.3% Fe; the chalcopyrite was the main copper-bearing mineral, but the pyrite was the main sulphidic mineral in this ore
№ 2	Mixed oxide-sulphidic copper ore also from the Vlaikovvrah deposit, with 0.32% Cu, 3.0%S, 4.8% Fe; several copper-bearing oxides (cuprite, tenorite, chalcosite) and sulphides (mainly covellite and chalcopyrite)were present
№ 3	Sulphidic copper ore from the Elshitza deposit, with 0.55% Cu, 7.3% S, 6.4% Fe; the chalcopyrite, chalcosite and covellite were the main copper-bearing minerals
№ 4	Copper-pyrite ore from the Chelopetsh deposit, with 0.62% Cu, 9.6% S, 8.2% Fe; the tenantite, chalcopyrite and lusonite were the main copper-bearing minerals in the ore which contained about 21% pyrite
№ 5	Copper-molibdenic ore from Elatzite deposit, with 0.36% Cu, 0.55% S, 1.95% Fe, 0.005% molibdenite; the chalcopyrite, was the main copper-bearing mineral
№ 6	Mixed copper ore from the Tsar Assen deposit, with 0.29% Cu, 1.16% S, 3.2% Fe; the chalcopyrite and cmalachite were the main copper-bearing minerals

Samples from these ores were subjected to bioleaching experiments performed by the shake-flask technique and by leaching in percolation columns. The bioleaching in flasks was performed by using from 5 to 20 g of ore with a particle size of minus 200 microns and 100 ml of the 9K nutrient medium used as a leach solution in Erlenmeyer flasks of 350 ml each. The duration of leaching was up to 14 days (336 hours) at different temperatures (from 10 to 50^{o}C).

The bioleaching of the ore samples was performed also in plastic cylindrical columns. Each of the columns was 220 cm high, with a diameter of 105 mm and contained 30 kg of the ore, with a particle size of minus 10 mm. The duration of leaching was 300 days at temperatures varying from 10-14 to 18-28^{o}C.

Elemental analysis was done by atomic adsorption spectrometry and inductively coupled plasma spectrometry. The isolation, identification and enumeration of microorganisms were carried out by means of the classical physiological and biochemical tests (Karavaiko et al., 1988) and by the molecular PCR methods (Sanz and Köchling, 2007; Escobar et al., 2008).

Results and Discussion

The microflora of the six copper ores deposits used in this study was dominated by acidophilic chemolithotrophic bacteria related to the species *Acidithiobacillusferrooxidans, At. thiooxidans, At. acidophilus* and *Leptospirillumferrooxidans*. The bacteria from the species *At. ferrooxidans* possessed both iron and sulphuroxidising abilities and were the prevalent microorganisms in most copper deposits studied in this investigation. Their numbers in some rich-in-pyrite zones extended 10^{8} cells/g ore. Regardless of the ability of these bacteria to oxidise the ferrous iron and the different forms of sulphur (the sulphidic, elemental and sulphitic) to sulphate, the mixed cultures of these bacteria with some strains of the typical sulphur-oxidiser *At. thiooxidans* were the most efficient during the leaching of sulphide minerals.

Data about the microbial leaching of copper from the ores used in this study are shown in Tables 2-5.

Table 2. *Bioleaching of the copper ores by the shake-flasks technique using mesophilic bacteria*

Ore samples	Number of the strains	Cu extraction, %
№ 1	6	68.0 – 81.5
№ 2	4	73.5 – 92.3
№ 3	5	64.4 – 79.0
№ 4	4	61.7 – 77.0
№ 5	6	60.8 – 84.2
№ 6	5	77.0 – 93.2

Leaching conditions: 20 g from each ore with a particle size minus 200 microns were leached in 100 ml 9K nutrient medium in flasks of 300 volume for 10 days (240 hours) at 35^{o}C.

It was found that the different chemolithotrophs even such related to one and the same taxonomic species, can differ considerably from each other with respect to this ability. The most efficient oxidisers were some strains of extreme thermophilic archaea of the species *Sulfolobusmetallicus* and *Thermoplasmaacidophilum* at 86^{o}C but at relatively low pulp densities (up to 6-8%). Other strains from these species and of the *Metallosphaerasedula* were the most efficient at relatively higher pulp densities (10-15%) at 75^{o}C.

Table 3. *Bioleaching of the ore samples in plastic columns*

Ore samples	Source of the ore	Cu extraction, %
№ 1	Vlaikovvrah	77.4
№ 2	Vlaikovvrah	84.2
№ 3	Elshitza	80.6
№ 4	Chelopetch	79.0
№ 5	Elatzite	82.8
№ 6	Tsar Assen	86.4

Each columnwas 220 cm high, with an internal diameter of 105 mm, containing 30 kg of ore each, with a particle size of minus 10 mm; duration of leaching 300 days at 21-23^{o}C.

Table 4. *Bioleaching of the copper ores by the shake flasks technique using moderate thermophilic bacteria*

Ore samples	Number of the strains	Cu extraction, %
№ 1	4	77.4 – 86.4
№ 2	5	93.6 – 95.0
№ 3	5	75.2 – 84.0
№ 4	4	73.0 – 81.5
№ 5	6	92.5 – 96.1
№ 6	4	93.0 – 97.0

Leaching conditions: The same as these mentioned in Table 2 but at 50°C.

Table 5. *Bioleaching of the copper ores by the shake flasks technique using extreme thermophilic archaea*

Ore samples	Number of the strains	Cu extraction, %
№ 1	5	73.0 – 84.6
№ 2	3	82.4 – 91.8
№ 3	4	70.9 – 82.8
№ 4	3	68.0 – 79.0
№ 5	5	84.0 – 86.4
№ 6	4	77.6 – 84.0

Leaching conditions: The same as these mentioned in Table 2 but at 75°C and 10% pulp density.

The study of the different oxidative abilities of strains related to one and the same taxonomic species is essential for the efficient selection of microorganisms suitable for the biotechnological treatment of the relevant mineral substrates. At the same time, it is also essential to evaluate correctly the economical values of the real technological processes connected with the microbial participation.

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